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(54) [Title of the Invention] TWO-LIQUID AQUEOUS NAIL LACQUER

(57) [Abstract] (Amended)

[Constitution] Two-liquid fingernail lacquer characterized by the fact that it consists of a base coat finger nail lacquer containing a vinyl polymer emulsion in which the glass-transition temperature of the constituent polymer is -50 to 20°C and an overcoat fingernail lacquer containing a vinyl polymer emulsion in which the glass-transition temperature of the constituent polymer is 0 to 180°C, the glass-transition temperature of the constituent polymer of the base coat finger nail lacquer being at least 10°C lower than that of the constituent polymer of the overcoat.

[Effect] The two-liquid aqueous nail lacquer of the invention provides good gloss, adhesion, water resistance, film strength, and the like that cannot be obtained with the prior art single vinyl polymer emulsions. This is accomplished by using at least two vinyl polymer emulsions with a difference of at least 10°C in *T<sub>g</sub>* where the low-*T<sub>g</sub>* polymer emulsion is used as the base coat and the high-*T<sub>g</sub>* polymer emulsion is used as the overcoat. The advantages of this nail lacquer include the fact that it is nonflammable and free of solvent odor. Consequently, it can be widely used in place of the prior art nail lacquers consisting primarily of organic solvents.

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## [Claims]

[Claim 1] Two-liquid fingernail lacquer characterized by the fact that it consists of a base coat fingernail lacquer containing a vinyl polymer emulsion in which the glass-transition temperature of the constituent polymer is  $-50$  to  $20^{\circ}\text{C}$  and an overcoat fingernail lacquer containing a vinyl polymer emulsion in which the glass-transition temperature of the constituent polymer is  $0$  to  $180^{\circ}\text{C}$ , the glass-transition temperature of the constituent polymer of the base coat fingernail lacquer being at least  $10^{\circ}\text{C}$  lower than that of the constituent polymer of the overcoat.

## [Detailed Description of the Invention]

[0001]

[Industrial Field of Application] The present invention concerns two-liquid nail lacquers. More specifically, it concerns a two-liquid nail lacquer consisting primarily of water and using polymer emulsions with different glass-transition temperatures. The term nail lacquer as used in the present invention encompasses nail enamels, nail enamel base coats, and nail enamel overcoats.

[0002]

[The Prior Art and Its Problems] Nail lacquers such as nail enamels, nail enamel base coats, and nail enamel overcoats are widely used to color, adorn, and prevent damage to nails.

[0003] The most common prior art nail lacquers consist primarily of film-forming agents such as nitrocellulose and alkyd resins, plasticizers, and organic solvents.

Although these organic solvent-based lacquers have excellent properties as film-forming agents, because of the use of organic solvents, they also have serious drawbacks, such as inflammability, a solvent odor, and effects on the human organism, particularly on the nails. In order to overcome these drawbacks, aqueous nail lacquers in which organic solvents are not used have been developed and disclosed in recent years.

[0004] For example, Unexamined Japanese Patent Application Disclosure Tokkai No. Sho 54-28836 and Examined Japanese Patent Application Tokko No. Sho 55-43445 disclose nail lacquers consisting of acrylic polymer emulsions, but the present inventors' studies have revealed, for example, that they are difficult to apply by brush and have poor film-forming ability (especially at low temperatures) and that the applied films have poor gloss.

[0005] Tokkai Nos. Sho 56-131513 and Sho 57-56410 disclose nail lacquers consisting of acrylic polymer microemulsions, but a drawback of the resulting films is their complete brittleness under mechanical wear.

[0006] Tokkai Nos. Sho 56-131513 and Sho 62-63507 disclose peelable aqueous nail lacquers which are rendered impractical by the drawback that they peel off under the conditions of everyday wear.

[0007] Since all of these nail lacquers use as film-forming agents polymer emulsions, emulsion-polymerized using a water-soluble

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natural or synthetic macromolecule and an emulsifying agent, and since the film substances themselves have poor water resistance, it is difficult for them to perform well as nail lacquers under the rigors of practical use.

[0008]

[Means of Solving the Problems] In view of this situation, the present inventors conducted rigorous studies aimed at obtaining aqueous nail lacquer having advantages such as good gloss, adhesion, water-resistance, and film strength, as well as being nonflammable and free of solvent odor.

[0009] As a result, they discovered that this objective could be achieved by a two-liquid aqueous nail lacquer consisting of a combination of two vinyl polymer emulsions with different glass-transition temperatures, using the emulsion with the higher glass-transition temperature as the overcoat and the emulsion with the lower glass-transition temperature as the base coat.

[0010] Thus, the present invention provides a two-liquid fingernail lacquer characterized by the fact that it consists of a base coat fingernail lacquer containing a vinyl polymer emulsion in which the glass-transition temperature of the constituent polymer is  $-50$  to  $20^{\circ}\text{C}$  and an overcoat fingernail lacquer containing a vinyl polymer emulsion in which the glass-transition temperature of the constituent polymer is  $0$  to  $180^{\circ}\text{C}$ , the glass-transition temperature of the constituent polymer of the base coat fingernail lacquer being at least  $10^{\circ}\text{C}$  lower than that of the constituent polymer of the overcoat.

[0011] In the present invention, two vinyl polymer emulsions are used: a vinyl polymer emulsion with a relatively low glass-transition temperature ( $T_g$ ) of at least  $-50$  to  $20^{\circ}\text{C}$  (hereinbelow, "low- $T_g$  emulsion") and a vinyl polymer emulsion with a relatively high  $T_g$  of  $0$ - $180^{\circ}\text{C}$ , which is at least  $10^{\circ}\text{C}$  higher than the  $T_g$  of the low- $T_g$  emulsion (hereinbelow, "high- $T_g$  emulsion").

[0012] The high- $T_g$  and low- $T_g$  emulsions are polymer emulsions which satisfy the respective  $T_g$  conditions hereinabove and are obtained by polymerizing or copolymerizing vinyl monomers such as acrylic acid and methacrylic acid.

[0013] Examples of acrylic acid monomers include acrylic acid, methyl acrylate, ethyl acrylate, *n*-propyl acrylate, isopropyl acrylate, *n*-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, and *N,N*-dimethylaminoethyl acrylate. Examples of methacrylic acid monomers include methacrylic acid, methyl methacrylate, ethyl methacrylate, *n*-propyl methacrylate, isopropyl methacrylate, *n*-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, hydroxyethyl methacrylate, and *N,N*-dimethylaminoethyl methacrylate.

[0014] Examples of vinyl monomers other than these acrylic acid or methacrylic acid monomers include styrene, acrylonitrile, methacrylonitrile, vinyl chloride, vinylidene chloride, vinyl acetate, methyl vinyl ether, ethyl vinyl ether, *n*-propyl vinyl ether,

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isopropyl vinyl ether, *n*-butyl vinyl ether, isobutyl vinyl ether, and *N,N*-dimethylaminopropylacrylamide.

[0015] The  $T_g$  (°K) of copolymers can be calculated with the following formula.

$1/T_g = W_1/T_{g1} + W_2/T_{g2} + \dots T_{g1}, T_{g2}, \dots$ : The  $T_g$  (°K) of the homopolymer of each monomer in each composition.

$W_1, W_2, \dots$ : The weight fraction of each component.

°K: Absolute temperature

[0016] As mentioned hereinabove, the difference in the  $T_g$ s of the high- $T_g$  emulsion and low- $T_g$  emulsion used in the invention is at least 10°C, but a difference of at least 20°C is preferred.

[0017] Examples of manufacturing methods include known methods of emulsifier-free polymerization of the desired monomers, mentioned hereinabove, such as soap-free polymerization using a reactive emulsifying agent and heterogeneous polymerization in an aqueous medium not containing an emulsifying agent.

[0018] An example of a particularly preferred method consists of solution-polymerizing these monomers in a hydrophilic organic solvent that is miscible with water and has a lower boiling point than water such as methyl ethyl ketone or a lower alcohol and then adding water and removing the organic solvent to obtain a polymer emulsion.

[0019] In addition, it is also possible to use a multilayered complex polymer emulsion manufactured by conducting multistage seed polymerization. When a complex polymer emulsion is used, the designated  $T_g$  in the invention refers to the  $T_g$  of the external layer of the complex emulsion. In this case, it is preferred for the  $T_g$  of the internal layer of the complex emulsion to be, for example, at least 50°C.

[0020] The base coat nail lacquer and overcoat nail lacquer constituting the two-liquid aqueous nail lacquer of the invention are prepared by blending, as film-forming agents, vinyl polymer emulsions which satisfy the respective  $T_g$  conditions, named hereinabove, by conventional methods.

[0021] The amount of vinyl polymer emulsion blended into the base coat and overcoat nail lacquers is 5-60 percent, by weight (hereinbelow, simply %, meaning solids). If less than 5% is used, several coats are necessary in order to obtain the type of film needed in practical use. If more than 60% is used, the nail lacquer increases in viscosity, becoming more difficult to apply, for example, by brush.

[0022] It is preferred to add film-forming aids and plasticizers to both nail lacquers used in the present invention. Film-forming aids and plasticizers are substances that lower the film-forming temperature, examples including ethylene glycol, propylene glycol, pentaerythritol, glycerol, liquid paraffin, chlorinated paraffin, machine oil, dioctyl phthalate, dibutyl phthalate, tricresyl phosphate, Cellosolve, butyl Cellosolve, Cellosolve acetate,

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Carbitol, butyl Carbitol, Carbitol acetate, butyl Carbitol acetate, Texanol, xylene, hexylene glycol, benzyl alcohol, phenol, 1,3-butyleneglycol, dipropylene glycol, and isoprene glycol.

[0023] It is preferred to add these film-forming aids and plasticizers in amounts of 0-25 parts, by weight, per 100 parts of vinyl polymer emulsion, 3-20 parts, by weight, being more preferred.

[0024] Pigments, dyes, preservatives, fragrances, viscosity builders, and the like can be added to the nail lacquer of the invention as desired. Examples of pigments include, in particular, conventional organic pigments such as R-221, R-226, R-220, B-1 Al lake, and Y-4 Al lake. In addition to such organic coloring agents, inorganic substances such as titanium dioxide, brown oxide, red oxide, and cloud white bismuth titanium oxychloride.

[0025]

[Effect of the Invention] The two-liquid aqueous nail lacquer of the invention obtained in the manner described hereinabove provides good gloss, adhesion, water resistance, film strength, and the like which cannot be obtained with the prior art single vinyl polymer emulsions. This is accomplished by using at least two vinyl polymer emulsions with a difference of at least 10°C in  $T_g$  where the low- $T_g$  polymer emulsion is used as the base coat and the high- $T_g$  polymer emulsion is used as the overcoat. The advantages of this nail lacquer include the fact that it is nonflammable and free of solvent odor. Consequently, it can be widely used in place of the prior art nail lacquers consisting primarily of organic solvents.

[0026]

[Working Examples] The present invention is described in further detail hereinbelow by means of synthesis examples and working examples; however, it is in no way limited by these examples.

[0027] Synthesis Example 1

Synthesis of polymer emulsion A: 50 parts of methyl ethyl ketone was charged to a reactor equipped with an agitator, reflux condenser, dropping funnel, thermometer, and pipe for introducing nitrogen gas, and the dissolved oxygen was removed in a stream of nitrogen gas. Meanwhile, 35 parts of methyl ethyl ketone, 41.5 parts of methyl methacrylate, 50.0 parts of *n*-butyl acrylate, 8.5 parts of *N,N*-dimethylaminoethyl methacrylate, and 0.2 parts of azobisisobutyronitrile were charged to the dropping funnel. During agitation, the temperature in the reactor was raised to 80°C, and the above-named monomers and the free-radical initiator (methyl ethyl ketone solution) were added dropwise from the dropping funnel over a period of 2.5 hours. Two hours after the addition of the monomers was completed, a solution of 0.2 parts of azobisisobutyronitrile dissolved in 10 parts of methyl ethyl ketone was added. After aging at the same [80°C] temperature for 3 hours, another solution of 0.1 parts of azobisisobutyronitrile dissolved in 5 parts of methyl ethyl ketone was added, and the

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reaction was continued for another 5 hours to give a copolymer. [0028] Upon completion of the reaction, the copolymer solution was cooled to room temperature and neutralized by the addition of 4.5 parts of lactic acid. 300 parts of deionized water was added while agitating at 300 rpm, and the methyl ethyl ketone was vacuumed off at 40°C and the water at 50°C to obtain a copolymer. The resultant copolymer (polymer emulsion A) contained 30% solids and had a  $T_g$  of 0°C.

## [0029] Synthesis Example 2

Synthesis of polymer emulsion B: A monomer composition consisting of 49 parts of methyl methacrylate, 42.8 parts of *n*-butyl acrylate, and 8.2 parts of *N,N*-dimethylaminoethyl methacrylate was copolymerized in methyl ethyl ketone, using the same method as in Synthesis Example 1. Next, a copolymer was obtained by neutralizing this copolymer with the addition of 4.5 parts of acetic acid and inverting to the aqueous phase by the same method as in Synthesis Example 1. The resultant copolymer (polymer emulsion B) had a solids content of 30% and  $T_g$  of 10°C.

## [0030] Synthesis Example 3

Synthesis of polymer emulsion C: 130 parts of water, 73 parts of methyl methacrylate, 23 parts of *n*-butyl acrylate, 4 parts of acrylic acid, 20 parts of (28%) aqueous ammonia, and, as a polymerization initiator, 0.05 parts of ammonium persulfate were charged to a 300-mL four-necked flask and polymerized at 65°C in a nitrogen stream for 3 hours while agitating at 300 rpm. The mixture was then dialyzed through cellophane paper to remove ionic impurities, giving polymer emulsion C. The resultant polymer emulsion C had a solids content of 35% and a  $T_g$  of 50°C.

## [0031] Synthesis Example 4

Synthesis of polymer emulsion D: A monomer composition consisting of 62 parts of methyl methacrylate, 34 parts of butyl acrylate, and 4 parts of acrylic acid was copolymerized by the same method as in Synthesis Example 3. The resultant polymer emulsion D had a solids content of 35% and a  $T_g$  of 30°C.

## [0032] Working Example 1

A two-liquid aqueous nail lacquer was prepared from the following formulation by conventional methods.

## Formulation:

(Base Coat Nail Lacquer)

Polymer emulsion A

 $(T_g 0^\circ\text{C})$ 

Pigment (Red pigment R-221)

Deionized water

Carbitol

Diethyl phthalate

Hydroxyethylcellulose

Fragrance

Preservative

100 parts

3 parts

10 parts

10 parts

5 parts

1 part

0.1 part

0.1 part

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Silicone antifoaming agent

0.1 part

[0033] [Overcoat Nail Lacquer]

Polymer emulsion C

 $(T_g 50^\circ\text{C})$ 

100 parts

Deionized water

10 parts

Carbitol

10 parts

Diethyl phthalate

5 parts

Hydroxyethylcellulose

0.5 part

Fragrance

0.1 part

Preservative

0.1 part

Silicone antifoaming agent

0.1 part

[0034] Working Example 2

A two-liquid aqueous nail lacquer was prepared from the following formulation by conventional methods.

## Formulation:

(Base Coat Nail Lacquer)

Polymer emulsion A

 $(T_g 0^\circ\text{C})$ 

100 parts

Pigment (Red pigment R-221)

1 part

Deionized water

10 parts

Carbitol

10 parts

Diethyl phthalate

5 parts

Hydroxyethylcellulose

1 part

Fragrance

0.1 part

Preservative

0.1 part

Silicone antifoaming agent

0.1 part

[0035] (Overcoat Nail Lacquer)

Polymer emulsion C

 $(T_g 50^\circ\text{C})$ 

100 parts

30 Pigment (Red pigment R-221)

3 parts

Deionized water

10 parts

Carbitol

10 parts

Diethyl phthalate

5 parts

Hydroxyethylcellulose

1 part

Fragrance

0.1 part

Preservative

0.1 part

Silicone antifoaming agent

0.1 part

[0036] Working Example 3

An aqueous nail lacquer was prepared from the following formulation by conventional methods.

## Formulation:

(Base Coat Nail Lacquer)

Polymer emulsion B

 $(T_g 10^\circ\text{C})$ 

100 parts

Pigment (Red pigment R-221)

1 part

Deionized water

10 parts

Carbitol

10 parts

Diethyl phthalate

5 parts

Hydroxyethylcellulose

1 part

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Fragrance	0.1 part
Preservative	0.1 part
Silicone antifoaming agent	0.1 part
[0037] (Overcoat Nail Lacquer)	
Polymer emulsion D	
(T <sub>g</sub> 30°C)	100 parts
Deionized water	10 parts
Carbitol	10 parts
Diethyl phthalate	5 parts
Hydroxyethylcellulose	0.5 part
Fragrance	1 part
Preservative	0.1 part
Silicone antifoaming agent	0.1 part

## Working Example 4

A two-liquid aqueous nail lacquer was prepared from the following formulation by conventional methods.

## Formulation:

(Base Coat Nail Lacquer)

Polymer emulsion B	
(T <sub>g</sub> 10°C)	100 parts
Pigment (Red pigment R-221)	2 parts
Deionized water	10 parts
Carbitol	10 parts
Diethyl phthalate	5 parts
Hydroxyethylcellulose	1 part
Fragrance	0.1 part
Preservative	0.1 part
Silicone antifoaming agent	0.1 part

[0039] (Overcoat Nail Lacquer)

Polymer emulsion D	
(T <sub>g</sub> 30°C)	100 parts
Pigment (Red pigment R-221)	2 parts
Deionized water	10 parts
Carbitol	10 parts
Diethyl phthalate	5 parts
Hydroxyethylcellulose	1 part
Fragrance	0.1 part
Preservative	0.1 part
Silicone antifoaming agent	0.1 part

[0040] Comparative Example 1

An aqueous nail lacquer was prepared from the following formulation by a conventional method.

## Formulation:

Polymer emulsion A

(T <sub>g</sub> 0°C)	100 parts
Pigment (Red pigment R-221)	3 parts
Deionized water	10 parts
Carbitol	10 parts
Diethyl phthalate	5 parts
Hydroxyethylcellulose	1 part
Fragrance	0.1 part
Preservative	0.1 part
Silicone antifoaming agent	0.1 part

[0041] Comparative Example 2

An aqueous nail lacquer was prepared from the following formulation by a conventional method.

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## Formulation

Polymer emulsion C

(T <sub>g</sub> 50°C)	100 parts
Pigment (Red pigment R-221)	3 parts
Deionized water	10 parts
Carbitol	10 parts
Diethyl phthalate	5 part
Hydroxyethylcellulose	1 part
Fragrance	0.1 part
Preservative	0.1 part
Silicone antifoaming agent	0.1 part

[0042] Testing

The nail lacquers obtained in Working Examples 1-4 and Comparative Examples 1 and 2 were evaluated for drying properties, gloss, adhesive properties, water resistance, wear resistance, and odor. The results are shown in Table 1.

[0043] (Evaluation Methods)

(1) Drying properties

Specimens were applied to nails with a nail enamel brush under conditions of 25°C temperature and 60% relative humidity, and the time for the samples to dry to the touch was measured. The base coat and overcoat nail lacquers of the two-liquid nail lacquers of the invention were evaluated separately.

○: Less than 3 minutes

△: 3 to 6 minutes

×: More than 6 minutes

[0044] (2) Gloss

The gloss of the dried films was evaluated visually 30 minutes after the evaluation of drying properties. The base coat compositions were covered with the overcoat compositions of the working examples, and two coats of the compositions of the comparative examples were applied for this evaluation.

[0045] (3) Adhesive properties

Adhesive properties were evaluated 30 minutes after the evaluation of drying properties by scraping off the dried film with a microspatula. The base coat compositions were covered with the overcoat compositions of the working examples, and two coats of the compositions of the comparative examples were applied for this evaluation.

[0046] (4) Water Resistance

Specimens were uniformly applied to nylon plates, 0.5 × 15 × 40 mm in size, with a nail enamel brush, dried for 1 hour at a temperature of 25°C and relative humidity of 60%, and immersed in 35°C water for 1 hour for evaluation of deterioration (clouding, swelling, softening, peeling, etc.). The base coat compositions were covered with the overcoat compositions of the working examples, and two coats of the compositions of the comparative examples were applied for this evaluation.

[0047] (5) Wear Resistance

The condition of the dried films was observed after rubbing 50 times with a cotton cloth 30 minutes after the drying properties were evaluated. The base coat compositions were covered with the overcoat compositions of the working examples, and two coats of the compositions of the comparative examples were applied for this evaluation.

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[0048] (6) Odor

The odor at the mouth of the nail enamel bottle was subjected to sensory evaluation. The base coat and overcoat lacquers of the two-liquid aqueous nail lacquers of the invention were evaluated separately.

[0049] Test items (2) to (6) were evaluated on the following scale.

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◎ : Excellent

○ : Good

△ : Fair

× : Poor

[0050] (Results)

[Table 1]

Table 1

	Working Examples						Comparative Examples	
	1		2		3		1	2
	Base Coat	Overcoat	Base Coat	Overcoat	Base Coat	Overcoat		
Drying properties	◎	○	◎	◎	◎	○	○	○
Gloss	○	○	○	○	○	○	○	○
Adhesive properties	◎	◎	◎	◎	○	○	△	×
Water Resistance	○	○	○	○	◎	◎	×	×
Wear Resistance	○	○	○	○	○	○	△	×
Odor	○	○	○	○	○	○	○	○

As can be clearly seen from these results, the two-liquid aqueous nail lacquer of the invention is superior to the prior art in terms of adhesive properties, water resistance, wear resistance, and the like.